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(54) ROOM TEMPERATURE-CURABLE COMPOSITION

(57)Abstract:

PURPOSE: TO provide a composition suitable as a sealing agent and curable in rubber-like state by water content.

CONSTITUTION: A room temperature-curable composition comprises (A) a hydrolyzable silicon group-containing polymer containing a hydrolyzable silicon group obtained by introducing $\text{SiCH}_3(\text{OCH}_3)_2$ group to the ends of a linear polyoxypropylenepolyol which is obtained by adding propylene oxide to an initiator such as glycerol and an organic carboxylic acid salt of bismuth compound of 1 pts.wt. based on 100 pts.wt component A, and a room temperature- curable composition further added thereto 0.3 pts.wt. caprylic acid or lauric amine. A cured product having excellent elongation is obtained therefrom.

* NOTICES *

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2 **** shows the word which can not be translated.

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CLAIMS

[Claim(s)]

[Claim 1] A hydrolytic silicon group content polymer (A) which contains one hydrolytic silicon group even if small per one molecule of polymers, and a room-temperature-curing nature constituent which contains ten or less weight sections of bismuth compounds (B) to (A)100 weight sections.

[Claim 2] A hydrolytic silicon group content polymer (A) which contains one hydrolytic silicon group even if small per one molecule of polymers, and a room-temperature-curing nature constituent which contains ten or less weight sections of alkalis (C) for a bismuth compound (B) to ten or less weight sections and (A)100 weight section to 100 weight sections.

[Claim 3] A room-temperature-curing nature constituent of claim 1 or claim 2 whose hydrolytic silicon group is a silicon functional group expressed with a following general formula.

- SiX₃R_{3-n} (as for a univalent hydrocarbon group or a halogenated hydrocarbon group, and X, in the beside of a formula, and R, a hydrolytic basis and a are the integers of 1, 2, or 3)

[Claim 4] A room-temperature-curing nature constituent of claim 1 or claim 2 whose hydrolytic silicon group content polymers are the molecular weights 2000-50000.

[Claim 5] A room-temperature-curing nature constituent of claim 1 or claim 2 whose bismuth

compound is an organic-carboxylic-acid salt of bismuth.

[Claim 6] A room-temperature-curing nature constituent of claim 5 whose organic-carboxylic-acid salt of bismuth is bismuth tris (2-ethylhexoate) or bismuth tris (neo decanoate).

[Claim 7] A room-temperature-curing nature constituent of claim 2 whose acid is organic carboxylic acid.

[Claim 8] A room-temperature-curing nature constituent of claim 2 whose alkali is organic amine.

[Translation done.]

例	1	2	3	4	5	6	7	8
重合体の種類	A	A	A	A	B	C	D	A
熱硬化化合物の種類	E	E	F	F	E	E	E	C
酸値・塩基性物質	一級基	酸	酸	酸	酸	強基	強基	強基
引 伸 率 (%)	2.1	2.3	2.1	2.4	3.5	4.3	3.7	2.2
引 伸 率 (kg/cm ²)								
試 験 条件 (kg/cm ²)	9.8	11.6	10.9	11.3	10.3	9.8	12.3	9.1
結 果	720	770	700	750	400	230	400	480
伸 長 率 (%)	84	87	83	87	93	95	90	88
伸 長 率 (時間 %)								
伸 長 率 (時間 %)	85	90	86	92	95	97	83	90

[0057]

[Effect of the Invention] The hardenability constituent which has physical properties outstanding by this invention is obtained. Elongation is improved as compared with what uses a tin compound as a catalyst especially conventionally.

[Translation done.]

diethylsulfonamide, Triethylsulfonamide, tetraethylsulfonamide, a butylamine, hexylamine, octylamine, decyl amine, lauryl amine, Hexamethylenediamine, heptamethylenediamine, dibutyl amine, Diethylenetriamine, N,N,N'-tetraethylenetriamine, 1,3-bisazabicyclohexane, Benzylamine, dimethylallylamine, dimethylamine ethanol, N,N,N'-triethylamine, triethylamine, N,N'-diethylamine, dimethylallyl amine, etc. can be used.

[0013]As a hydroxylic silicon group content polymer (A) of this invention, various polymers which have one or more hydroxylic silicon groups in the main chain, and in which a main chain consists of heteroatoms, are particularly suitably used. A compound specifically indicated in the following description is mentioned.

[0014]For example, a hydroxylic silicon group content polymer which introduced a hydroxylic silicon group into JP46-12514B, JP3-47825A, and JP3-72521A by a method which is stated to an end of a polysiloxane compound below is indicated.

[0015]A polymer of polyolol which has at the end the hydroxylic silicon group combined with JP45-38319B by specific bond groups, or a polyester system is indicated.

[0016]JP3-79627A, which introduced a hydroxylic silicon group into a copolymer of monooxepoxide, such as allylene oxide, and unsaturation group content monooxepoxide, such as allyl glycidyl ether, is indicated.

[0017]Furthermore, Alkylene oxide, such as propylene oxide, is added to hydroxyl group and polybutadiene. To a polymer obtained, a hydroxylic silicon group. A hydroxylic silicon group content polymer (refer to the Japanese-Patent-Application-No. 11 05881, two to 1) specification in connection with application of these people) of the molecular weights 300-30000 can be used with a polymer chain which main chains, such as what was introduced, have the residue of liquid rubber and/or hydrogenation liquid rubber, and has a polyether chain.

[0018]As for a main chain of a hydroxylic silicon group content polymer (A), what consists of polysiloxane chain intrinsically or a polysiloxane chain in a side chain is preferred. A hydroxylic silicon group content polymer introduces a hydroxylic silicon group into a compound which has such polysiloxane chain and has a function group which has polysiloxane chain. Monooxepoxide, such as JP37-08944, etc., is made to react to initiators, such as a hydroxy compound which has at least one hydroxyl group under existence of catalysts, such as an alkaline metal catalyst, a composite metal cyanide complex catalyst, and metallophyrin, and it is manufactured. As for a functional group number of a compound which has polysiloxane chain, two or more are preferred, and 2 or 3 is especially preferred.

[0019]Especially a desirable compound is a compound which has a polyoxypropylene chain and has two pieces or three hydroxylic groups. Specifically, it is a propylene oxide adduct of polyoxypropylene diol, polyoxypropylene triol, liquid rubber, and/or hydrogenation liquid rubber, etc.

[0020]When using for a method of following (1), a polysiloxane compound of olefin ends, such as an allyl and polyoxypropylene monomer, can also be used.

[0021]As a hydroxylic silicon group introduced into a compound which has the above-mentioned polysiloxane chain, a silyl group expressed with a general formula (a) is good.

$$-SiR_3R_4R_5 \dots (a)$$

[0022]The inside R of a formula is a univalent hydrocarbon group or a halogenated hydrocarbon group, and eight or less carbon number is six or less alkyl group and a fluoro alkyl group preferably. They are low-grade alkyl groups, such as a methyl group and an ethyl group, especially preferably.

[0023]As a hydroxylic basis, for example, there are a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOXSHI mate group. As for a carbon number of a hydroxylic basis which has a carbon atom among these, six or less are preferred, and four lower alkyl or less are preferred. Desirable hydroxylic bases are a with a carbon number of four or less epoxy group, especially a preferred hydroxy and an ethoxy basis.

[0024]As for a silyl group expressed with a general formula (a), it is preferred to average in a total terminal group and to contain not less than 70% preferably not less than 50%.

[0025]Although a method in production of a compound which has polysiloxane chain of a silyl group expressed with a general formula (a) is not limited, it can be introduced, for example by the following methods.

[0026](1) A method to which a hydroxylic compound expressed with an end of a compound which has polysiloxane chain (b) by a general formula (b) that an olefin group was introduced is made to react.

$$[O_2]3HSiR_3R_4R_5 \dots (b)$$

It is the same as the above the inside R, X, and a of a formula)

[0027]As a method of introducing an olefin group here, A compound which has an unsaturation group and a functional group is made to react to terminal hydroxy group of a compound which has polysiloxane chain. How to combine by either bond, ester bond, a urethane bond, carbonate bond, imidation, etc., or when polymerizing alkylene oxide, a method of introducing an olefin group into a side chain, etc. are mentioned by an allyl glycidyl ether.

[0028](2) A method to which a compound expressed with an end of a compound which has polysiloxane chain by a general formula (c) is made to react.

$$R_3R_4R_5-SiX_3R_6NCO \dots (c)$$

(It is the same as the above the inside R, X, and a of a formula.) R¹ is a divalent hydrocarbon group of the carbon numbers 1-17.

[0029](3) A method to which W basis of a silicon compound expressed with a general formula (d) to this isooctanoate group is made to react after mixing polysiloxane compounds, such as toluene diisocyanate, react to an end of a compound which has polysiloxane chain and considering it as an isooctanoate group end.

$$[O_3]4R_3R_4R_5-SiX_3R_6R_7W \dots (d)$$

(The inside R of a formula, R¹, X, and a are the same as the above.) Active hydrogen containing group which W was chosen from a hydroxyl group, a carboxyl group, a sulfonyl group, an amino group (the 1st class or the 2nd class).

[0030](4) A method which introduces an olefin group into an end of a compound which has polysiloxane chain and to which the olefin group and a sulfonyl group of a silicon compound expressed with a general formula (d) whose W is a sulfonyl group are made to react.

[0031]If a hydroxylic silicon group content polymer (A) in this invention contains moisture, it will three-dimensionalize by crosslinking reaction, and it will be hardened.

[0032]As for a molecular weight of a hydroxylic silicon group content polymer (A) in this invention, 2000-50000, especially 5000-50000 are preferred, and 16000-30000 are the most preferred.

[0033]The constituent of this invention can contain further various bulking agents, an additive agent, etc. Although general things such as calcium carbonate, kaolin, talc, titanium oxide, aluminum silicate, or carbon black, are mentioned as a bulking agent, especially in order to speed up hardening, add system bulking agents, such as kaolin and aluminum silicate, are preferred.

[0034]When using for a method of following (1), a polysiloxane compound of olefin ends, such as an allyl and polyoxypropylene monomer, can also be used.

[0035]As a hydroxylic silicon group introduced into a compound which has the above-mentioned polysiloxane chain, a silyl group expressed with a general formula (a) is good.

$$-SiR_3R_4R_5 \dots (a)$$

[0036]The inside R of a formula is a univalent hydrocarbon group or a halogenated hydrocarbon group, and eight or less carbon number is six or less alkyl group and a fluoro alkyl group preferably. They are low-grade alkyl groups, such as a methyl group and an ethyl group, especially preferably.

[0037]As a hydroxylic basis, for example, there are a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOXSHI mate group. As for a carbon number of a hydroxylic basis which has a carbon atom among these, six or less are preferred, and four lower alkyl or less are preferred. Desirable hydroxylic bases are a with a carbon number of four or less epoxy group, especially a preferred hydroxy and an ethoxy basis.

[0038]As for a silyl group expressed with a general formula (a), it is preferred to average in a total terminal group and to contain not less than 70% preferably not less than 50%.

[0039]Although a method in production of a compound which has polysiloxane chain of a silyl group expressed with a general formula (a) is not limited, it can be introduced, for example by the following methods.

[0040](1) A method to which a hydroxylic compound expressed with an end of a compound which has polysiloxane chain (b) by a general formula (b) that an olefin group was introduced is made to react.

$$[O_2]3HSiR_3R_4R_5 \dots (b)$$

It is the same as the above the inside R, X, and a of a formula)

[0041]As a method of introducing an olefin group here, A compound which has an unsaturation group and a functional group is made to react to terminal hydroxy group of a compound which has polysiloxane chain. How to combine by either bond, ester bond, a urethane bond, carbonate bond, imidation, etc., or when polymerizing alkylene oxide, a method of introducing an olefin group into a side chain, etc. are mentioned by an allyl glycidyl ether.

[0042](2) A method to which a compound expressed with an end of a compound which has polysiloxane chain by a general formula (c) is made to react.

$$R_3R_4R_5-SiX_3R_6NCO \dots (c)$$

(It is the same as the above the inside R, X, and a of a formula.) R¹ is a divalent hydrocarbon group of the carbon numbers 1-17.

(Polymer A) The organic polymer which introduced the $-SO_3H(OCH_3)_2$ group into the end of the linear polyoxypropylene polyol of the molecular weight 17000 to which dipropylene glycol was made to add propylene oxide by the method given in JP3-72827A.

[0045](Polymer B) The organic polymer which introduced the $-SO_3H(OCH_3)_2$ group into the end of the linear polyoxypropylene polyol of the molecular weight 22000 to which glycerin was made to add propylene oxide by the method given in JP3-72827A.

[0046](Polymer C) The organic polymer which introduced the $-SO_3H(OCH_3)_2$ group into the linear polyoxypropylene polyol of the molecular weight 10000 to which dipropylene glycol was made to add propylene oxide by the method given in JP3-47825A.

[0047](Polymer D) By the method of a statement, to JP2-110888A. The organic polymer which introduced the $-SO_3H(OCH_3)_2$ group into the end of the conversion oxypropylene compound of the molecular weight 10000 which made propylene oxide add to hydrogenation polyisoprene system polyol (seals made from the demiteu petrochemistry; the molecular weight 2400, the average functional group number 2.2).

[0048]The example of the hardenability constituent prepared below using above-mentioned polymer A-D is shown. Examples 1-7 show an example and Example 8 shows a comparative example.

[0049]To polymer 100 weight sections each shown in Table 1, [Example 1] Calcium carbonate 140 weight section, After kneading DOP30 weight section, titanium oxide 20 weight section, hydrogenation castor oil 6 weight section, and antiaging agent 1 weight section by the system in which moisture does not exist substantially, one weight section of curing catalysts shown in Table 1 were added, it kneaded uniformly, and the hardenability constituent was obtained.

[0050][Examples 2-8] Except adding acid or alkali 0.3 weight section shown in Table 1 with a curing catalyst, the same operation as Example 1 was performed, and the hardenability constituent was obtained.

[0051]When H type specimen was produced according to JIS-A5756 and it was recuperated for 14 days under 23 ± 2 ° and 80% humidity atmosphere using the constituent obtained in Examples 1-8, the rubber-like elasticity object which hardened thoroughly to the inside in any case was acquired.

[0052]The result of having examined by pulling at the rate of 30 mm/min about these is shown in Table 1.

[0053]The result of having set these hardened materials in the state of 50 ± 2 ° and 30% compression continuously for 24 hours, and having canceled the set continuously, and having measured the recovery is collectively shown in Table 1.

[0054]The curing catalyst and acid which were used in Examples 1-8, and an alkali are as follows.

(Curing catalyst)

Catalyst compound E: Bismuth tris (2-ethylhexanoate)

Catalyst compound F: Bismuth tris (two decanoate)

Catalyst compound G: 2-ethylhexanoic acid tin

[0055](The acid or alkali)

Acid: Caprylic acid

Alkali: Lauryl amine

[0056]

[Table 1]

例	1	2	3	4	5	6	7	8
重合体の種類	A	A	A	A	B	C	D	A
触媒化合物の種類	E	E	E	F	E	E	E	G
酸・塩基性物質	—	塩基	酸	塩基	塩基	塩基	塩基	塩基
引張強試験	50%モジュラス (kg/cm ²)	2.1	2.3	2.1	2.4	3.5	3.7	2.2
試験								
硬断強度 (kg/cm ²)	9.8	11.6	10.9	11.3	10.3	9.8	12.3	9.1
結								
果								
伸び (%)	720	770	700	750	400	230	400	480
復元率								
3時間後 (%)	84	87	83	87	93	95	90	86
24時間後 (%)	85	90	86	92	95	97	93	90

[0057]

[Effect of the Invention]The hardenability constituent which has physical properties outstanding by the invention is obtained. Elongation is improved as compared with what uses a tin compound as a catalyst especially conventionally.

[Translation done.]